

Structure, elastic properties and strength of amorphous and nanocomposite carbon

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Abstract

We study theoretically the equilibrium structure, as well as the response under external load, of characteristic carbon-based materials. The materials considered include diamond, amorphous carbon (a-C), “amorphous diamond” and nanocomposite amorphous carbon (na-C). A universal bulk modulus versus density curve is obeyed by all structures we consider. We calculate the dependence of elastic constants on the density. The strength of a-C was found to increase in roughly a linear manner, with increasing concentration of four-fold atoms, with the maximum stress of the strongest a-C sample being about half that of diamond. The response of na-C to external load is essentially identical to the response of the embedding a-C matrix.

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1. Introduction

Amorphous carbon (a-C) is a well-established carbon-based material, with distinct mechanical properties such as hardness and thermal stability. These properties render a-C to be an ideal material for coating applications. Recently, nanocomposite carbon (na-C) has been synthesized in both hydrogenated and pure forms [1]. It is considered as a material with similar, and perhaps better properties than those of a-C. Na-C consists of nanometer-scale regions of crystalline material embedded into an a-C matrix. This material has mechanical properties between those of a-C and diamond [2] that could in principle be fine-

tuned by adjusting either the size of the nanocrystalline region or the density of the amorphous matrix. Such tailoring of material properties to match those desired in the applications could be invaluable.

The properties of a-C and na-C can be categorized into two broad classes: The first class includes macroscopic, mean-field properties, such as the density, that are implicitly only related to individual chemical bonds. Atomistic properties, on the other hand, such as the strength, arise directly from the individual chemical bonds between C atoms of different electronic structure. The macroscopic properties are usually related to the minimum or the harmonic regime of the cohesive energy versus volume curve, and can, therefore, be easily calculated using any reasonable description for the bonds. On the other hand, even a rough estimate of atomistic properties requires employing some level of quantum theory.

A quantum-mechanical treatment is able to accurately describe the chemical bond, but can only be used to study few hundreds of atoms for very short time scales. On the other hand, a classical empirical potential method can handle three

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orders of magnitude more atoms for realistic time scales, at the price of a limited accuracy in the description of the chemistry of carbon. This interplay between classical and quantum-mechanical simulations has been used to verify or predict several experimental findings for na-C: diamond nanocrystallites were found to be stable, having negative formation energy, when the amorphous matrix is dense [3]. The average intrinsic stress of the material is zero [4]. Although the bulk modulus of na-C is higher than that of a-C, the two materials have identical ideal strength due to identical fracture mechanisms [2]. In this work, we first establish the validity of our simulations by ensuring that different approximations yield identical qualitative and similar quantitative results. We then study in more detail the elastic properties of these materials, including the dependence of elastic moduli as a function of their density. Finally, we comment on their behavior under strain well beyond the elastic regime, and discuss briefly their fracture.

2. Computational method

The quantum-mechanical calculations are based on two different tight-binding Hamiltonians. The so-called NRL-TB was developed by Papaconstantopoulos et al. at the Naval Research Laboratory [5]. The parametrization of the Hamiltonian for C is based on similar assumptions to the previously published parametrization for Si; see Ref. [6] for a review. The environment-dependent tight-binding (EDTB) model of Wang et al. [7] goes beyond the traditional two-center approximation and allows the TB parameters to change according to the bonding environment. In this respect, it is a considerable improvement over the previous two-center model of Xu et al. [8]. Both NRL-TB and EDTB schemes have been used successfully to simulate a-C systems [9,2]. The tight-binding molecular-dynamics simulations are carried out in the canonical (N, V, T) ensemble, T being controlled via a stochastic temperature control algorithm. The supercells used in the tight-binding simulations contain 512 C atoms each.

The empirical potential simulations are based on the continuous-space Monte Carlo method. We employ the many-body potential of Tersoff [10], which provides a very good description of structure and energetics for a wide range of carbon-based materials [11,12]. This method allows for great statistical accuracy, as it is possible to have samples at full thermodynamic equilibrium. Moreover, through the use of relatively large supercells, it offers the possibility to explore a larger portion of the configurational space of the problem. The supercells used in the Monte Carlo simulations contain 4096 C atoms each.

Na-C is modeled by a periodic repetition of cubic supercells that consist of a spherical crystalline region surrounded by a-C. To construct such supercells, we first consider a cubic supercell of diamond, and choose the radius of the spherical crystalline phase. Keeping the atoms inside this sphere frozen to their diamond lattice positions, we run the system at a very high temperature (12,000–15,000 K) so that a liquid is created, and then quench it down to 50 K, at constant volume. After that, the system is fully equilibrated by relaxing both the system volume

and the coordinates of all atoms. In the Monte Carlo simulations, we perform an additional intermediate relaxation at room temperature to ensure that the sample is fully relaxed.

By adjusting the volume or, equivalently, the pressure of the liquid phase, we can create samples having low- or high-density a-C. It has been shown that properties of a-C can be described in terms of a single parameter, z [9]. This is the average coordination number, or number of neighbors, for each atom in the sample. More precisely, z is the integral of the nearest-neighbor peak of the pair-correlation function. By convention, individual atoms in a-C are thought of having an electronic structure in one-to-one correspondence to their coordination number: four-, three- and two-fold atoms are usually labeled in the literature as sp^3 , sp^2 and sp^1 , respectively. Although for most atoms such a relationship between coordination number and hybridization holds to a good approximation, other atomic electronic structures may be present as well. We create samples with average coordination between 3.1 and 3.9, having concentrations of four-fold coordinated atoms between 10 and 90%. Samples with $z > 3.8$ are considered as tetrahedral amorphous Carbon (ta-C). We also consider the fully tetrahedral Wooten–Winer–Weaire (WWW) structure [13], as a model for “amorphous diamond”. The radius of the nanocrystalline region is of the order of 2 nm (1 nm for the quantum-mechanical simulations), while it occupies about 30–40% of the total volume, in accordance to experimental observations [14].

3. Equilibrium structural properties

Structural properties of diamond, “amorphous diamond” and a-C are summarized in Table 1. For diamond, we calculate the density (ρ) and the bulk modulus (B) using the two tight-binding schemes and the Tersoff potential. All methods yield results in good agreement to experiment. The a-C samples we considered consist mostly of four- and three-fold atoms, while two-fold atoms appear in low-density samples. Using the EDTB model, we had found that the density of a-C depends linearly on z , via $\rho \approx -3.3 + 1.7z$ [9]. We find that the linear relationship

Table 1
Structural properties of diamond (D), “amorphous diamond” (WWW) and four characteristic a-C samples (A–D)

	z	N_4	N_3	N_2	B	ρ	ρ^{fit}
D	4.0	100	0	0	480	3.7	
D (E)	4.0	100	0	0	428	3.5	
D (T)	4.0	100	0	0	422	3.5	
D (e)	4.0	100	0	0	443	3.5	
WWW	4.0	100	0	0	434	3.4	3.5
A	3.8	78	22	0	387	3.1	3.2
B	3.7	67	32	1	361	2.9	3.0
C	3.5	47	52	1	325	2.5	2.7
D	3.2	18	77	5	211	1.6	2.1

All samples are simulated using NRL-TB, except D (E), D (T) and D (e) that contain results obtained from the EDTB, Tersoff potential and experiment, respectively. N_4 , N_3 and N_2 is the percentage of four-, three- and two-fold atoms, respectively. B is the bulk modulus (in GPa), ρ the calculated density (in g/cm^3), and ρ^{fit} is the density (in g/cm^3) according to the fit of ρ vs. z from Ref. [9].

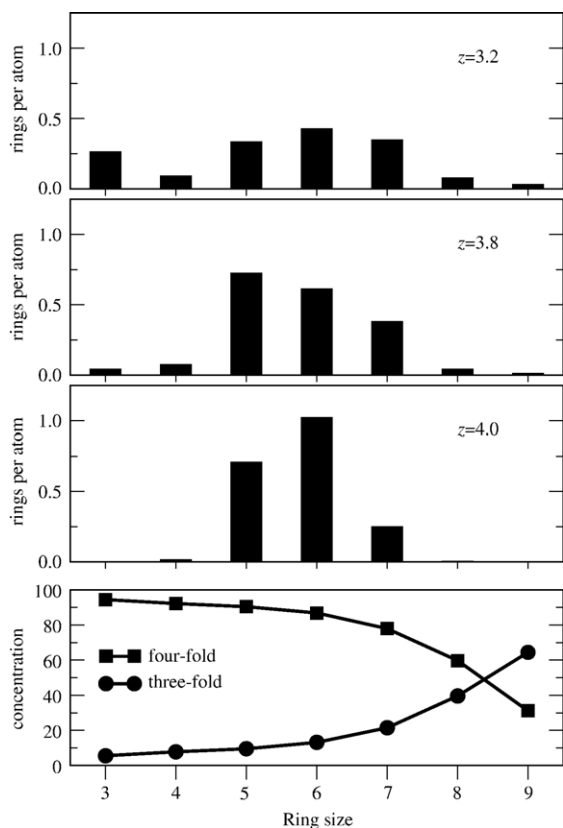


Fig. 1. Ring statistics for various a-C samples, as calculated using the NRL-TB. The upper three panels show the number of rings divided by the total number of atoms in the sample, as a function of the number of atoms participating in each ring, for three cases: low-density a-C ($z=3.18$), ta-C ($z=3.78$) and “amorphous diamond” ($z=4.00$). Lowest panel shows the concentration of rings in four-fold and three-fold atoms for the ta-C sample.

found using EDTB is also valid within NRL-TB, at least for the denser samples.

Insight into the atomistic structure of a-C can be gained by looking at the sizes and distributions of rings of atoms in the material. A ring having k members is defined as a path which, starting from a given atom, returns to itself after passing through k atoms. Rings of atoms are defined in terms of the shortest-path criterion of Franzblau [15]. The number of atoms that participate in a ring is the ring size, and can have only specific values for a bulk crystalline material: in diamond, for example, the smallest ring size is six. On the contrary, three-member rings are common in a-C. As the formation of rings is related to atomistic binding, a quantum-mechanical treatment is necessary in order to get reliable ring statistics.

Results for the relative ring numbers and concentrations, found using the NRL-TB for three characteristic samples, are shown in Fig. 1. Similar results have been obtained with EDTB [9]. For the low-density sample, we find significant numbers for three- and four-member rings, while the most probable ring length is six. For ta-C, the most probable ring length is five, while there are still some three- and four-member rings. Finally, for the “amorphous diamond” sample, most rings are six-membered, with few five- and seven-member ones. Although, by construction, only four-fold atoms exist in this sample, its

random topology allows for rings that would not be present in the crystalline material.

The bottom panel of Fig. 1 shows the composition of rings as a function of their size, for the ta-C sample. Most atoms (over 90%) of the smallest rings are four-fold. The concentration of four-fold atoms decreases with increasing ring size; for large rings, with more than eight members, most atoms are three-fold. This behavior can be attributed to the long-range correlations found for π -bonded atoms; such π bonds are more likely to occur between three- than between four-fold atoms. On the other hand, such double bonds are more difficult to bend in order to form triangles or quadrangles; this is why most atoms that participate in small rings are four-fold. 85% of the three-member rings and 75% of the four-member rings consist of four-fold atoms only, while there are no rings of sizes 8 and above having only four-fold atoms. The ring statistics presented here are in excellent agreement to experiments and state-of-the-art *ab initio* simulations [16,17].

A typical sample of na-C, generated in the NRL-TB scheme is shown in Fig. 2. The volume fraction of the nanocrystalline region is 31%. The surrounding amorphous material is ta-C ($z=3.8$ and $\rho=3.0$ g/cm³). A sample created using EDTB under identical conditions has the same crystal volume fraction and a-C coordination, and only slightly higher density of the amorphous phase, 3.1 g/cm³. In all cases, the surrounding a-C matrix obeys the same density vs. coordination relationship as pure a-C samples generated using the same recipe. The a-C atoms are covalently bonded to the crystal, resulting thus in thin interface regions.

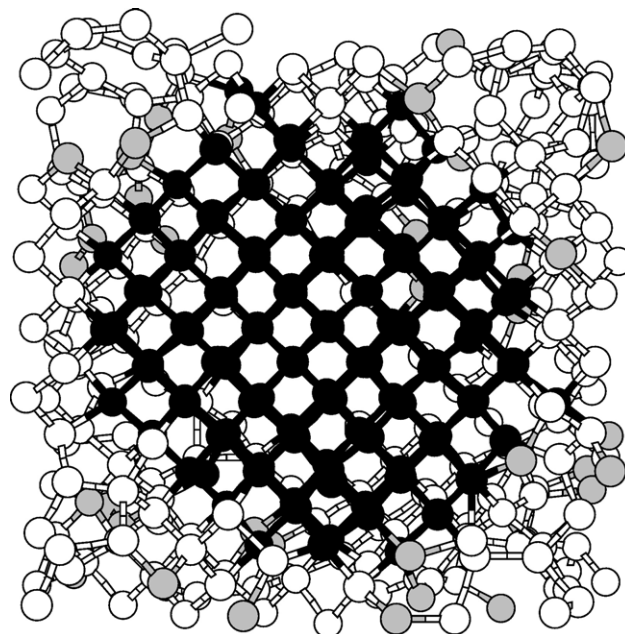


Fig. 2. Cross-section of a ball-and-stick representation for a typical model structure of nanocomposite amorphous Carbon created using EDTB: a spherical nanocrystal with a diameter of 1.24 nm is embedded into amorphous-C with an average coordination of 3.8. Atoms belonging to the crystal are represented by black spheres; four- and three-fold atoms of the amorphous matrix are represented by white and gray spheres, respectively.

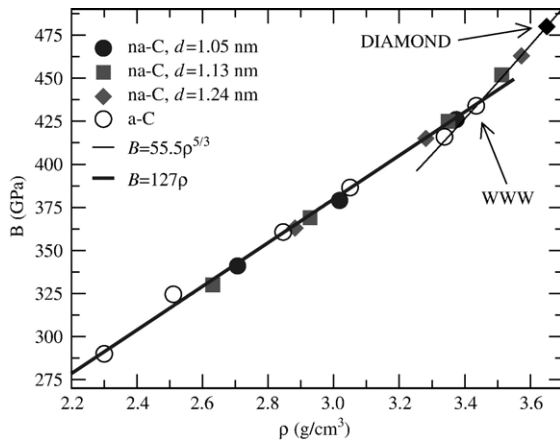


Fig. 3. Bulk modulus as a function of density, calculated within NRL-TB, for na-C with different radii of the crystalline region. Calculations for a-C of various densities, bulk diamond and “amorphous diamond” are also shown.

As a first estimate of the hardness of nanocomposite carbon-based materials, we calculated their bulk modulus, B . In Fig. 3, we plot B as a function of the total density of the samples, ρ . The bulk modulus of na-C is enhanced compared to that of pure a-C [2]. Replacement of some amorphous material by crystalline increases noticeably the bulk modulus, rendering it for some samples to be higher even than that of the “amorphous diamond”, and close to that of diamond [2].

Interestingly, all samples, including pure a-C, na-C, WWW, and even diamond, seem to follow the same universal curve in Fig. 3. Such universalities have been observed in the past: He and Thorpe [18] showed that $B \sim (z - z_0)^{1.5}$, where z_0 is universal; Liu et al. [19] showed that $B \sim d^{-3.5}$, where d is the average distance between atoms. Recently, Mathioudakis et al. [9] showed that the two approaches are equivalent, and that for a-C, $B \sim (d - \text{const.})^{-3.5}$. The last relationship would imply that $B \sim (\rho^{-1/3} - \text{const.})^{-3.5}$. Indeed, this function provides an alternative fit of the a-C data of Fig. 3 [9] for the whole range of densities. The calculated bulk moduli are in general in very good agreement to the measured ones. The agreement is better for higher densities; for example, the calculated bulk modulus of a-C for $z=3.9$ coincides with Surface Brillouin Scattering experiments [9].

The universal dependence of B on ρ can be understood by considering the microscopic response of the material to the external pressure. We can think of two regimes: in low-density materials, the pressure is undertaken by appropriately adjusting the volume of the void regions of the material. Such voids exist in every low-density material and are a result of induced dipole (van der Waals) interactions. On the other hand, for dense materials, strong covalent bonds have to be deformed, resulting in higher bulk moduli. In this case, the resistance of the electrons to compression follows from their quantum nature and the Pauli principle.

In the first case, the scaling of B with respect to ρ can be found by considering a model solid bonded exclusively through van der Waals interactions. Using the Lennard–Jones potential we can find that $B \sim \rho$ [20]. On the other hand, for high densities, we can get the correct scaling by using the free-electron approximation:

in this case, $B \sim \rho^{5/3}$ [20]. This picture is demonstrated in Fig. 3: $B \sim \rho$ for $\rho < 3.3 \text{ g/cm}^3$, while $B \sim \rho^{5/3}$ for $\rho > 3.3 \text{ g/cm}^3$. These relationships hold with surprisingly good accuracy.

Being such a fundamental average property, the B vs. ρ curve should be reproduced well by both our tight-binding models and the empirical potential, as the latter is known to reproduce correctly the elastic response of the material. On the other hand, the density dependence of elastic constants associated with changes in shape, like the Young’s modulus, can be different. Although the response of materials to volume changes can be addressed at almost any level of theory, understanding the response to shape changes requires a model that takes into account the directionality of the chemical bonds. Fortunately, as the calculation of elastic constants require only small deformations from the minimum energy structure, the empirical potential approach should suffice for their calculation. As the Monte Carlo simulations offer greater statistical accuracy and refer to more realistic sizes of the crystalline regions, we prefer to employ this method for the calculation of elastic constants.

To calculate the elastic constants, we apply the appropriate deformation to the system and compute its total energy as a function of the imposed strain. The curvature of this function at its minimum yields the desired modulus. The number of independent elastic constants depends on the symmetry of the material: For a material with cubic symmetry, there are three independent elastic constants, while for an isotropic material, such as a-C or na-C, there are only two [21]. In Fig. 4 we plot c_{11} , c_{12} , c_{44} and the Young’s modulus Y as a function of density for na-C and diamond. All elastic constants increase with increasing density, similar to the previously described behavior of the bulk modulus as a function of density. For an isotropic material, $2c_{44} = c_{11} - c_{12}$. This relationship holds within 4% or less, for all data points presented in Fig. 4, demonstrating that na-C is a highly isotropic material. The moduli c_{11} and c_{44} are both associated with changes in shape, and this is why their values for na-C are much lower than the corresponding values

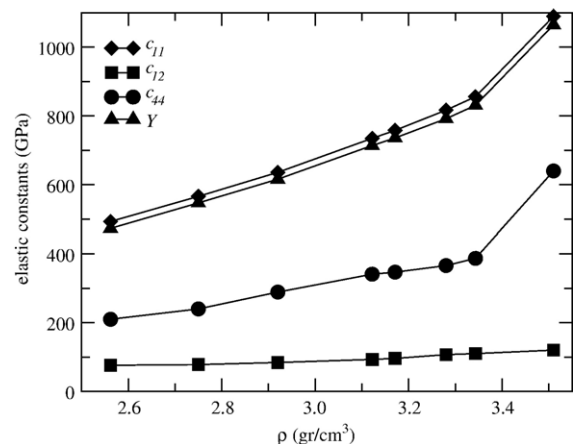


Fig. 4. Elastic constants of na-C, calculated using the Tersoff potential, as a function of the total density. The average diameter of the crystalline region is 1.7 nm, and the surrounding a-C matrix has $z=3.8$. The rightmost point for each data set, for a density $\rho=3.51 \text{ g/cm}^3$, corresponds to diamond and is taken from Ref. [11].

for diamond, where strong directional bonds are bent. On the other hand, c_{12} describes simultaneous elongation along two axes without shearing, and the value of this modulus for diamond follows the trend observed for na-C.

4. Ideal strength and fracture

The response of covalently-bonded materials, such as a-C and na-C, under strain can be categorized into three broad regimes: For small strains, the response of the material is elastic, and Hooke's law stands: the stress is proportional to the applied strain. For example, if tensile strain is applied to an isotropic material, the stress will equal the strain times the Young's modulus. The second regime corresponds to strain beyond the elastic limit, and is usually associated with plastic deformation of the material. The stress experienced by the material increases with increasing strain until a maximum stress (strength) is reached. The third regime is associated with strain beyond that giving the maximum stress. For brittle materials like diamond, the material breaks when the maximum stress is reached, and further increase of the strain results therefore in zero stress. Ductile materials, on the other hand, can be deformed beyond the strain corresponding to the maximum of the stress.

To study the strength of a-C and na-C, we apply tensile load on the [111] easy slip plane of the crystalline region. Strain is simply the ratio of the volume change divided by the initial volume of the sample; stress is the negative derivative of the energy with respect to volume. We consider three a-C samples: a typical a-C sample with average coordination $z=3.47$, a ta-C sample with $z=3.8$ and an "amorphous diamond" sample. As graphite ($z=3$) is known to be much softer than diamond ($z=4$), it is reasonable to expect that the strength increases with increasing z , as was the case for the elastic constants discussed in Section 3. This is observed in Fig. 5. The maximum stresses are roughly 60, 40 and 30 GPa for $z=4.00$, 3.78 and 3.50, respectively, so that the strength of a-C is roughly proportional

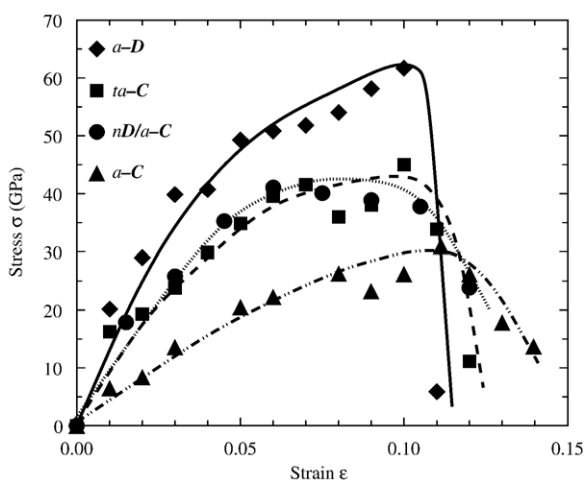


Fig. 5. Stress vs. strain curves for WWWW model of "amorphous diamond" (diamonds), ta-C (squares), low-density a-C (triangles) and na-C (circles). The latter consists crystalline regions of 1.2 nm surrounded by ta-C. Data shown are obtained by the NRL-TB method for tensile load in the (111) direction of the crystal.

to its concentration of four-fold atoms. Interestingly, the stress versus strain curve for the low-density a-C sample seems to suggest a ductile behavior. We get similar results when applying shear strain. As a-C is highly isotropic, the energy required to deform the material is a function of the change in its volume and does not depend much on how this change is applied.

The strength of diamond does not fit into the simple picture of the strength being proportional to the concentration of four-fold atoms. If that was the case, then the strength of the isotropic WWWW sample under tensile load would be higher than the strength of diamond under tensile load perpendicular to its easy slip plane, (111). After all, in the WWWW model the number of bonds per unit area for a given direction has to be higher than the number of bonds per unit area on the [111] plane of diamond. This justifies the name "easy slip plane" for the diamond (111). One could naively expect that the strength of the WWWW sample, consisting of four-fold atoms only, could perhaps be higher than that of diamond, due to the lack of such easy slip planes. On the contrary, the calculation reveals that the strength of diamond for tensile load along its easy slip direction, (111), is around 120 GPa, about twice that of the isotropic WWWW. Apparently, the lack of easy slip planes in WWWW is compensated by its somehow distorted bonds and the lack of order beyond the first-nearest-neighbor distance. Our results for diamond cleavage along [111], similar to the findings of Telling et al. [22], are not included in Fig. 5, for the benefit of the other curves' clarity.

We applied the same methodology to a na-C sample where crystalline regions having radii of about 1.2 nm are embedded in ta-C with a volume fraction of about 30%. The stress-strain curve for this sample follows exactly that of the embedding ta-C. The crystalline phase remains unaffected by the external load, which is almost completely taken by the surrounding amorphous matrix. Therefore, the response of na-C to external load beyond the elastic regime is identical to the response of the embedding matrix. As atoms in the amorphous matrix form bonds that are always weaker than the bonds in the crystal, the system prefers to stretch or bend these bonds and keep the strong diamond bonds untouched. By performing an atom-by-atom analysis of the deformation, we can probe the four-fold atoms of the amorphous atoms as the ones more extensively deformed when the material experiences large load [2].

5. Conclusions

We examined theoretically the structure, elastic and inelastic response to load of several carbon-based materials, including diamond, amorphous carbon (a-C) "amorphous diamond" (WWW) and nanocomposite amorphous carbon (na-C). These materials are formed by covalently-bonded four-fold and three-fold atoms and are characterized by their average coordination number (z). In a-C, three-, four- and five-member rings are formed, their number increasing with decreasing z . Most of such small rings contain four-fold atoms, while larger rings contain also three-fold atoms. The bulk modulus of all these carbon-based materials seems to follow a universal functional dependence of the density. All elastic constants were also found to increase with increasing density.

The strength of a-C was found to increase in roughly a linear manner, with increasing concentration of four-fold atoms. High-density sample exhibited a brittle behavior, analogous to that of diamond. The strongest a-C sample we considered was the “amorphous diamond” WWW sample; this has a maximum stress about half that of diamond. The response of na-C to external load is essentially identical to the response of the embedding a-C matrix.

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